Spectroscopic studies on MnO doped LiI–AgI–B$_2$O$_3$ glasses

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Abstract

LiI–AgI–B$_2$O$_3$ glasses mixed with different concentrations of MnO (ranging from 0 to 0.8 mol %) were synthesized. A variety of properties viz., electrical, dielectric and spectroscopic properties that include optical absorption, ESR and photoluminescence studies have been investigated.The valence states of manganese ions and their coordination in the glass network have investigated through optical absorption, luminesence and ESR spectroscopy . The analysis of spectroscopic results has indicated that the manganese ions exist in both Mn^{2+} and Mn^{3+} states and occupy octahedral and tetrahedral positions. With increasing MnO concentration there is a gradual increase in the tetrahedral occupancy of Mn^{2+} ions at the expense of octahedral occupancy in the glass network. The higher concentration of MnO and lower LiI content causes a strong cross link in the glass network. The value of optical band gap (Eo) is observed to increase gradually with the content of MnO in the glass network.The close examination of the g values obtained for the present glasses indicates the increasing covalent environment of Mn^{2+} ions with the increase in the concentration of MnO in the glass matrix. Luminescence studies indicate that with the increase in the concentration of MnO in the glass network, there is a gradual increase in the tetrahedral occupancy of Mn^{2+} ions at the expense of the octahedral ones.The differential thermal analysis of these samples has indicated an increase in thermal stability of glass against devitrification with increase in the concentration of MnO.

Keywords: LiI–AgI–B$_2$O$_3$ glasses: Manganese ions; Spectroscopic properties

Introduction:

In recent years there have been extensive investigations on the influence of manganese ions on electrical properties and other physical properties of various inorganic glass systems that include silicate, borate, arsenate, phosphate, tellurite etc. Manganese ions exist in different valence states with different coordinations in glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination where as in silicate and germinate glasses as Mn^{2+} with both tetrahedral and octahedral environment. Both tetrahedral and octahedral Mn^{2+} ions are reported to have exhibited luminescence emission in the green and red regions respectively in several glasses. Both Mn^{3+} and Mn^{2+} ions are well known paramagnetic ions. Mn^{3+} ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital where as such anisotropy energy of Mn^{2+} ion is small because its orbital angular momentum is zero.

When LiI-AgI-B$_2$O$_3$ glasses are doped with multivalent transition metal ions like manganese mixed electronic and ionic, pure electronic or pure ionic conduction is expected depending upon the composition of the glass constituents. Electronic conduction in this type of materials is predicted due to polaron hopping between different valent states

of manganese ions where as the ionic conduction is expected due to the diffusion of Li and Ag ions. The understanding of the charge carriers transport phenomenon in mixed ion-electron conducting glasses is a challenging and unsolved task because of the complexity of structure.

Glass Property ↓	$Mn_1 \rightarrow$	Mn_2	Mn_4	Mn_6	Mn_8
Density (g/cm³)	2.2551	2.2953	2.3101	2.4685	2.6821
Average molecular weight $\overline{M}$	96.25	96.20	96.06	95.94	95.81
Manganese ion concentration N_i (10^{20} ions/cm³)	0.141	0.287	0.579	0.929	1.34
Inter − ionic distance of Mn ions R_i ( )	41.37	32.64	25.83	22.06	19.49
Polaron radius R_p ( )	16.671	13.154	10.411	8.892	7.856
Field strength (10^{14}, cm⁻²)	0.719	1.155	1.845	2.529	3.239
Molar Vol. (cm³/mol)	42.67	41.91	41.66	38.86	35.72
Refractive index	1.650	1.651	1.652	1.652	1.655

The content of manganese in different environments and in different valence states existing in the glass however depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation, etc. Hence, the connection between the state and the position of the manganese ion and the electrical properties of the host glass containing highly mobile ions like Ag^+ and Li^+ is expected to be highly interesting.

In this chapter we have reported the results of the extensive investigations on electrical conductivity and dielectric properties over a wide frequency range from 0.01 Hz to 1 MHz and in temperature range from 173 to 523 K for $LiI–AgI–B_2O_3$ glasses doped with different concentration of MnO. The studies were also extended to spectroscopic properties viz., optical absorption, ESR and photoluminescence spectra so as to have some pre-assessment over the valance states of manganese ions and their coordination in the glass network; such

information will facilitate the analysis of the results of electrical properties quantitatively.Experimental

For the present study, a particular composition $(39–x)$ LiI –1.0Ag I–60 B_2O_3: xMnO with x ranging from 0 to 0.8 (in mol%) is chosen. The detailed compositions are as follows: n_0: 39 LiI–1.0 AgI–60 B_2O_3
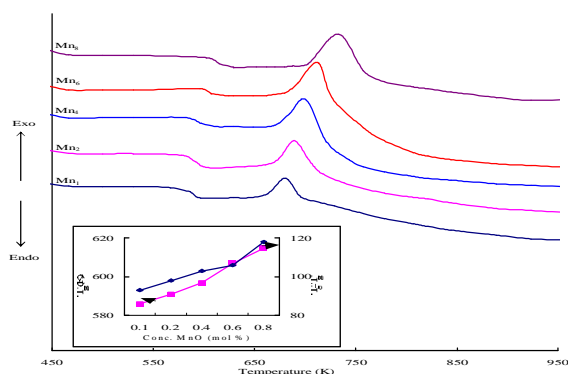
Mn_1: 38.9 LiI–1.0 AgI–60 B_2O_3: 0.1 MnO

Mn_2: 38.8 LiI–1.0 AgI–60 B_2O_3: 0.2 MnO

Mn_4: 38.6 LiI–1.0 AgI–60 B_2O_3: 0.4 MnO

Mn_6: 38.4 LiI–1.0 AgI–60 B_2O_3: 0.6 MnO

Mn_8: 38.2 LiI–1.0 AgI–60 B_2O_3: 0.8 MnO

Various physical parameters of LiI- AgI-B_2O_3 :MnO glasses

DSC Traces of LiI-AgI-B_2O_3 glass doped with different concentrations of MnO and inset shows the variation of the glass transition temperature T_g and T_c-T_g with the concentration of MnO

From the measured values of density, D, and calculated average molecular weight $\overline{M}$, various physical parameters such as manganese ion concentration N_i and mean manganese ion separation r_i for these glasses are determined using the conventional expressions and are presented in Table. The density of the glasses is found to increase considerably with the concentration of MnO. The increase of structural compactness, the modification of the geometrical configuration of the glassy network, changes in the coordination of the glass forming ions are the some of the factors that are responsible for the observed increase in the density.

DSC analysis

Fig. represents differential scanning calorimetric (DSC) curves of LiI–AgI–B_2O_3: MnO glasses. DSC traces indicate an inflection due to the glass transition

temperature T_g in the region from 586 to 615 K followed by a well defined exothermic effect due to the crystallization temperature (T_c) between 679 and 733 K. The glass transition temperature T_g and the parameter (T_c–T_g), a measure of thermal stability of glass against devitrification, increase with increase in the concentration of MnO (inset of Fig). Such trend indicates the increase of augmented cross–link density of various structural groups in the glass network and closeness of packing. ## Spectroscopic properties

Optical absorption

Fig. shows the optical absorption spectra of glasses in the wavelength region of 280-600 nm. The absorption edge observed at 381 nm for the glass M_1 is shifted gradually to a lower wavelength with increase in the concentration of MnO. The spectrum of this glass exhibited an intense absorption band at 523 nm corresponding to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ octahedral transition of Mn^{2+} ions; the spectrum also exhibited a weak kink at about 418 nm due to $^6A_1 (S) \rightarrow {}^4T_2 (G)$ tetrahedral transition of Mn^{2+} ions

Additionally a weak absorption band with a peak at about 498 nm due to $^5E_g \rightarrow {}^5T_{2g}$ octahedral transition of Mn^{3+} ions is also

observed in the spectrum of this glass. With increase in the concentration of MnO up to 0.8 mol %, the tetrahedral band is observed to grow gradually at the expense of the octahedral band with minor red shift. In general the Mn^{2+} ($3d^5$) complexes with five unpaired electrons are expected to occupy octahedral positions in the glass network.

However, the presence of these ions in tetrahedral positions is also reported in a number of glass systems The summary of data on the positions of various bands in the optical absorption spectra of LiI–AgI–B_2O_3: MnO glasses is presented in Table.The observed optical absorption bands are from the Mn^{2+} ion ground state
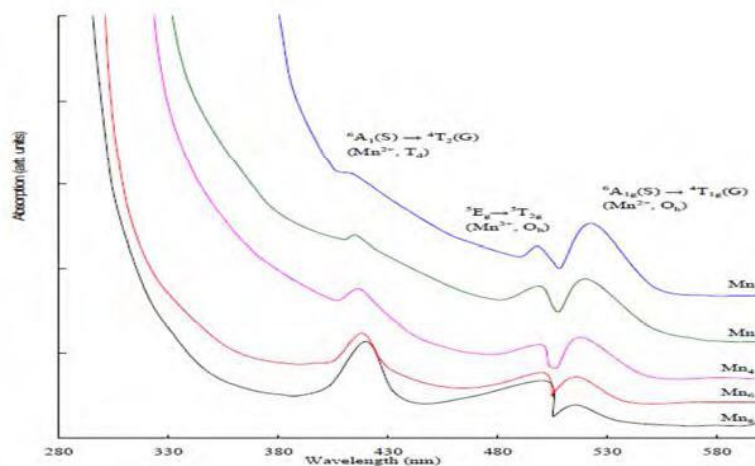
Optical absorption spectra of LiI-AgI - B_2O_3: MnO glasses recorded at room temperature

$^6A_{1g}$ to some quartet states and these are both spin and parity forbidden. The transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ involves a change of configuration from $(t_{2g})^3(e_g)^2$ to

$(t_{2g})^4(e_g)^1$ and is therefore observed to be comparatively broad. Since all the excited states are spin quartet states, no spin allowed transitions would occur for Mn^{2+} ions. Hence, Mn^{2+} ions are characterized by weak bands as observed which arise due to the spin forbidden transitions.

The appearance of a clear broad band in the spectra of the glasses at about 490 nm (due to spin allowed $^5E_g \rightarrow {}^5T_{2g}$ transition) indicates that a part of manganese ions exist in Mn^{3+} (d^4) and octahedral positions.From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Urbach plot between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$. The value of optical band gap (E_o) is observed to increase gradually with the content of MnO in the glass network.

Glasses	Mn_1	Mn_2	Mn_4	Mn_6	Mn_8
Mn^{2+}transitions (nm) (a) $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$	523.1	520.6	518.1	516.4	515.8
(b) $^6A_1(S) \rightarrow {}^4T_2(G)$	414.0	415.1	416.8	418.0	420.0
Mn^{3+} transition (nm) $^5E_g \rightarrow {}^5T_{2g}$	498.2	499.4	500.0	501.1	502.3
Cut-off wavelen (nm)	381	334	326	304	299
Optical band gap E_o (eV)	3.18	3.66	3.74	3.98	4.08

Summary of data on optical absorption of LiI-AgI-B$_2$O$_3$:MnO glasses.

The octahedrally positioned manganese ions similar to lithium and silver ions depolymerize the glass network by creating more bonding defects and non-bridging oxygens (NBOs). With the decrease in concentration of Mn^{2+} (O$_h$) (or increase in the concentration of tetrahedral ions) in the glass network, a decrease in the formation of donor centers is expected, and subsequently, the excited states of localized electrons originally trapped on Mn^{2+} sites begin to seperate with the empty 3d states on the neighboring Mn^{3+} sites, and as a result, the impurity or polaron band becomes less extended into the main band gap. This new polaronic development might have shifted the absorption edge to the higher energy, which leads up to a significant enlargement in the band gap as the concentration of MnO is increased.

ESR spectra

Fig. represents the typical ESR spectra of LiI–AgI– B$_2$O$_3$: MnO glasses. The spectra are characterized by six-line hyperfine structure centered at g ~ 2.005 and another signal at g ~ 4.3 The values of g obtained for Mn^{2+} ions in the present glass system is comparable with that of other systems; for example, Bi$_2$O$_3$ – GeO$_2$, lead phosphate, alkali sulphate glasses .

For Mn^{2+} ion, if we neglect the nuclear Zeeman term, the spin Hamiltonian term can be written as,

$$H = \mu_B gBS + ASI + DS_Z^2 - \frac{1}{3}S(S+1) + E(S_X^2 - S_Y^2)$$

Where μ_B is the Bohr magneton, g is electronic g factor, B is the Zeeman field, S is Mn^{2+} electronic spin =5/2, I is the Mn^{2+} nuclear spin = 5/2, A is the hyper fine interaction tensor and D and E are non-axial zero field splitting parameters..

In case of d^5 metal ions, it is known that the axial distortion of octahedral symmetry gives rise to three Kramers doublets $\left|\pm\frac{5}{2}\right\rangle, \left|\pm\frac{3}{2}\right\rangle$ and $\left|\pm\frac{1}{2}\right\rangle$ .An

application of Zeeman field will split the spin degeneracy of the Kramers doublets. As the crystal field splitting is normally much greater than the Zeeman field, the resonances observed are due to transitions within the Kramers doublets split by the Zeeman field. The resonance at g = 2.0 is due to Mn^{2+} ions in an environment close to an octahedral symmetry and is known to arise from the transition between the energy levels of the lower doublet $\left| \pm \frac{1}{2} \right\rangle$ .This line with

ell resolved hyperfine splitting (due to [55]Mn) can be further interpreted in terms of this spin-Hamiltonian described by Eq. by assuming that the parameters of the fine structure D and E are $|D| \cong |E| << $ g◻H, i.e., the non-cubic crystalline electric fields (that are contributing to the EPR spectra of these samples) are weak. The signal observed at g = 4.3 corresponding to $|D| \geq g\beta H$ and E/D = I/3 is due to magnetically isolated Mn^{2+} ions in tetragonally (and or rhombically) distorted octahedral sites of symmetry subjected to strong crystal field effects ,and arises from transitions between the energy levels of the middle Kramers doublet

Summary on ESR spectra of LiI-AgI-B₂O₃: MnO glasses.

 The intensity of the EPR signal is assumed to be proportional to the product of the peak-to-peak height (I) and the square of its width (◻B) [8]: $\Im \approx $ I (◻B)² The dependence of this factor, for $g_{eff} \approx 2.0$ resonance is shown as an inset of Fig. 5.4; the figure shows that the intensity of the resonance signal decreases with increase in the concentration of MnO. This may be either due to the decreasing presence of Mn^{2+} ions in octahedral distorted positions or due to increasing presence of trivalent manganese ions (as evidenced from optical absorption studies). The effective value of g obtained from ESR spectra show a gradual increase from 2.0027 (Table 5.3) with increase in the concentration of MnO in the glass matrix. This is partly ascribable to the contribution of orbital angular momentum to the magnetic moment of Mn^{2+} ions [41]. The value of g for hyperfine splitting may also give some information about the nature of the bonding with which the manganese ions participate in the glass network. The high is the shift in the g value towards positive side from 2.0023, the bonding is more covalent in nature [42]. The close examination of the g values obtained for the present glasses indicates the increasing covalent environment of Mn^{2+} ions with the increase in the concentration of MnO in the glass matrix.

Luminescence studies: The room temperature fluorescence spectra of LiI–AgI– B_2O_3: MnO glasses excited at the wavelength corresponding their absorption edge are shown in Fig.5.5; the spectrum of glass Mn_1 exhibited two emission bands at about 628 nm and 546 nm assigned to $^4G \rightarrow ^6S$ transitions .To be more tetragonally (and or rhombically) distorted octahedral sites of symmetry subjected to strong crystal field effects ,and arises from transitions between the energy levels of the middle Kramers doublet specific the 628 nm band is attributed to $^4T_{1g}(G) \rightarrow ^6A_{1g}(S)$

spin forbidden transition of octahedrally positioned Mn^{2+} ions where as the green emission band is identified due to $^4T_1$ (G) $\rightarrow ^6A_1$ (S) spin allowed transition of tetrahedrally positioned Mn^{2+} ions.

$^4G{\rightarrow}^6S$ transitions. To be more specific the 628 nm band is attributed to $^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ spin forbidden transition of octahedrally positioned Mn^{2+} ions where as the green emission band is identified due to $^4T_1 (G) \rightarrow {}^6A_1 (S)$ spin allowed transition of tetrahedrally positioned Mn^{2+} ions .

As the concentration of MnO is increased gradually up to 0.8 mol %, the tetrahedral band is observed grow at the expense of octahedral band. Thus the luminescence studies indicate that as the concentration of MnO increased there is gradual transformation of Mn^{2+} ions from octahedral to tetrahedral positions in the glass network.

Thus the summary of the results of spectroscopic studies is as follows: the manganese ions do exist in both Mn^{2+} and Mn^{3+} states in LiI–AgI– B_2O_3 glass network. Mn^{2+} ions occupy both octahedral and tetrahedral positions in the glass network. With the increase in the concentration of MnO in the glass network, there is a gradual increase in the tetrahedral occupancy of Mn^{2+} ions at the expense of octahedral occupancy.

Conclusions:

LiI–AgI–B_2O_3 glasses mixed withdifferent concentrations of MnO (ranging from 0 to 0.8 mol%) were synthesized. A variety of properties viz., electrical, dielectric and spectroscopic properties that include optical absorption, ESR, and photoluminescence studies have been investigated.

The differential thermal analysis of these samples has indicated an increase in thermal stability of glass against devitrification with increase in the concentration of MnO.

The optical absorption and ESR studies indicated that a part of manganese ions do exist in Mn^{2+} and Mn^{3+} state in these samples. The results of these studies along with luminescence spectral results have indicated that as the concentration of MnO increased there is gradual transformation of Mn^{2+} ions from octahedral to tetrahedral positions in the glass network.

Finally it is concluded that there is an increasing electrical rigidity (or insulating strength) of LiI–AgI– B_2O_3 glass samples with increase in the content of MnO in the glass network.

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